

12

EUROPEAN PATENT APPLICATION

21 Application number: 90810002.7

22 Date of filing: 04.01.90

51 Int. Cl.⁵: C08G 18/81, C08G 18/50,
C08G 18/38, C08G 18/10,
C08G 18/48, C08F 299/06,
G02B 1/04, C08G 65/32

30 Priority: 11.01.89 US 296169
11.01.89 US 296170

43 Date of publication of application:
25.07.90 Bulletin 90/30

84 Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

71 Applicant: CIBA-GEIGY AG
Klybeckstrasse 141
CH-4002 Basel(CH)

72 Inventor: Goldenberg, Merrill
626 Kent Avenue
Teaneck, N.J. 07666(US)

54 Vinylic macromers containing perfluoropolyalkylether and polyalkylether segments, polymers, copolymers and ophthalmic devices made therefrom.

57 The instant invention relates to vinylic macromers containing perfluoropolyalkylether and polyalkylether segments, polymers and ophthalmic devices such as intraocular implants and contact lenses and particularly soft hydrogel contact lenses made therefrom, and to crosslinked copolymers of (a) said vinylic macromers containing perfluoropolyalkylether and polyalkylether segments with (b) minor amounts of vinylic comonomers and ophthalmic devices such as intraocular implants and contact lenses and particularly soft hydrogel contact lenses made therefrom.

EP 0 379 462 A2

VINYLIC MACROMERS CONTAINING PERFLUOROPOLYALKYLETHER AND POLYALKYLETHER SEGMENTS, POLYMERS, COPOLYMERS AND OPHTHALMIC DEVICES MADE THEREFROM

The instant invention relates to vinylic macromers containing perfluoropolyalkylether and polyalkylether segments, polymers and ophthalmic devices, such as intraocular implants and contact lenses and particularly soft hydrogel contact lenses made therefrom and to crosslinked copolymers of (a) said vinylic macromers containing perfluoropolyalkylether and polyalkylether segments with (b) minor amounts of vinylic comonomers and ophthalmic devices such as intraocular implants and contact lenses and particularly soft hydrogel contact lenses made therefrom. These devices possess an advantageous blend of desirable properties including high oxygen permeability, excellent wettability, high mechanical strength, flexibility, optical clarity, biocompatibility, and capability of being sterilized in boiling water. The perfluoropolyalkylether segments provide in large part the high oxygen permeability, the polyalkylether segments provide the wettability and the unique polymer structure provides the desired mechanical properties.

In general, most existing hydrogel soft contact lens materials are based on HEMA, also known as 2-hydroxyethyl methacrylate or as ethylene glycol monomethacrylate, with one or more optional comonomers as described in U.S. Patent Nos. 2,976,576, 3,841,985 and 3,985,697. Other hydrogels based on N-vinylpyrrolidone copolymers and acrylamide copolymers are disclosed in U.S. Patent Nos. 3,639,524 and 3,929,741. These prior art hydrogel polymers generally suffer from several inherent problems being relatively weak mechanical strength, low dissolved oxygen permeability or a combination of both. Most lenses are made by either of two procedures, one requiring costly lathing and polishing steps and the other using delicate spin casting techniques where polymerization, crosslinking, and shaping are done simultaneously.

Perfluoropolyalkylether segments have been proposed as constituents of contact lens materials. For example:

In U.S. Patent Nos. 3,940,207 and 3,944,347 poly(perfluoropropylene oxide) oils were incorporated into a contact lens matrix. However, in this case the material is extremely hydrophobic and the oil can leach out.

In U.S. Patent No. 3,542,461 a terpolymer is formed from hexafluoroacetone, tetrafluoroethylene and ethylene. The polymers so formed are in general of insufficient wettability and some are not of complete clarity.

In U.S. Patent No. 4,440,918 and European Patent Application 084406, it is disclosed to make ophthalmic devices such as contact lenses from telechelic perfluorinated polyether polymers. These polymers are extremely hydrophobic and require the addition of a hydrophilic comonomer or surface treatment to improve wettability. Although an increase in wettability is described, the increase is generally insufficient to overcome the hydrophobic nature of the perfluoropolyether segments and to provide adequate patient comfort. Also, surface treatments are generally not permanent.

In Japanese Patent Applications 61-111308, 61-112047, 61-123609, 61-126052, 61-285425 and 61-285426, are described perfluoroalkylether containing polymers useful as raw materials for oxygen permeable devices and medical devices such as contact lenses. These polymers are of poor wettability and require the addition of hydrophilic comonomers or surface treatments to obtain the requisite wettability. Also some of these materials have a tendency of being yellow in color.

In European Patent Application 253515 is described the use of a perfluoropolyether monomer for use in soft contact lenses. These materials are also extremely hydrophobic and need a substantial quantity of hydrophilic comonomer to obtain wettability and in addition require the inclusion of the N-vinylpyrrolidone comonomer to obtain clarity.

Perfluoropolyether monomers useful in condensation polymerizations are disclosed in European Patent Application 084406 and Japanese Patent Application 61-166834. In the Japanese application a perfluoropolyether polytriazine material derived from a multivalent nitrile polymer is used in gas permeating materials such as contact lenses. These materials appear yellow in color. The perfluoropolyether monomers of both patent applications are hydrophobic and require the presence of a hydrophilic comonomer. In addition, condensation polymers are generally of poor quality for contact lens use because, for example, of the difficulty in obtaining a sufficiently high molecular weight with the concomitant desirable physical properties.

In European Patent Application 273449 are described aqueous dispersions of fluorinated polyurethanes containing ionic groups and their use for textile coatings.

It is an object of the present invention to overcome the disadvantages of the prior art by providing a modified perfluoropolyalkylether macromer which is inherently hydrophilic. This is accomplished by use of a block structure where the perfluoropolyalkylether block provides a substantial portion of the oxygen

permeability properties and the polyalkylether block provides the hydrophilicity.

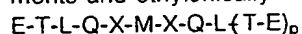
It is further object to provide a perfluoropolyalkylether/polyalkylether macromer which can be crosslinked in the absence or presence of a minor amount of another vinylic comonomer to form a soft water-swallowable hydrogel contact lens having high oxygen permeability, good wettability, high mechanical strength, flexibility, optical clarity, biocompatibility, and capability of being sterilized in boiling water. It is a further object of the present invention to provide medium to high water content contact lenses obviating, or substantially reducing, the drawbacks of the prior art.

It is further object of the present invention to provide a method of preparing such contact lenses by crosslinking a vinylic perfluoropolyalkylether/polyalkylether macromer in the absence or presence of a minor amount of another vinylic comonomer in a solvent in a mold, such as a spin cast mold or a static cast mold, and equilibrating the resulting solvent swollen crosslinked contact lens in an aqueous medium.

A further object of the invention is to provide a method of correcting visual defects in the form of refractive errors by fitting to the patient's eye in need of the same, a corrective contact lens of such polymer.

These and other objects of the invention are apparent from the following detailed description of the invention.

The instant invention provides a macromer containing perfluoropolyalkylether and polyalkylether segments and ethylenically unsaturated moieties, having the formula I,



wherein M denotes Z or G, p denotes zero or one and wherein Z is $-(C_aF_{2a}O)_b-CF_2-$, where a is 1 to 4 or a mixture thereof and b is 2 to 200;

X is a direct bond, $-CH_2-$, $-CH_2OCH_2CHOHCH_2-$, $-CH_2(OCH_2CH_2)_y-$ or carbonyl where y is 1 to 10;

Q is a direct bond, $-CONH-R-NHCO-$ or $-ACONH-R-NHCO-$ where A is oxa or imino and R is a divalent aliphatic group having from 2 to 14 carbon atoms, a divalent 5- or 6-membered cycloaliphatic group having 5 to 14 carbon atoms or an arylene group having 6 to 14 carbon atoms, and wherein the A of Q is attached to X;

L is $-A(C_mH_{2m}O)_nC_mH_{2m}AY$ or La , where Y is a direct bond when L is divalent or hydrogen when L is monovalent, and m is 2 to 4 or a mixture thereof and n is 5 to 100;

wherein A is as hereinbefore defined;

T is $-CONH-R_5A-$ or $-CONH-R-NHCOOR_5A-$ or $-CONH-R-NHCO-A-$ or $-R_5A-$ or a direct bond where A thereof is attached to E, where R_5 is alkylene or hydroxy-substituted alkylene of 2 to 15 carbon atoms and A and R are as hereinbefore defined;

E is $-CO-C(R_1)=CHR_2$ or $-CONH-phenyl-C(R_1)=CR_2H$ or $-CONH-C(R_4)_2-phenyl-C(R_1)=CHR_2$

where R_1 is hydrogen or methyl, and R_2 is hydrogen, methyl or $-COOR_3$,

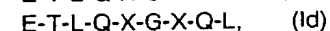
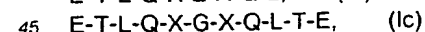
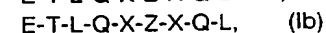
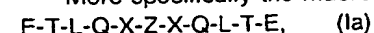
where R_3 is hydrogen or alkyl of 1 to 4 carbon atoms with the proviso that, when R_1 is methyl, R_2 is hydrogen; and wherein R_4 is hydrogen or methyl;

G is $-(C_aF_{2a}O)_b-CF_2[CH_2-OCONH-R-NHCOOCH_2CF_2(OC_aF_{2a})_b]_x-$ or $-(C_aF_{2a}O)_b-CF_2[CH_2-NHCONH-R-NHCONHCH_2CF_2(OC_aF_{2a})_b]_x-$ where x is 1 to 3; and a, b and R are as above; and

La is $-A(C_mH_{2m}O)_n[C_mH_{2m}ACONH-R-NHCOA(C_mH_{2m}O)_n]_zC_mH_{2m}AY$

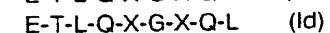
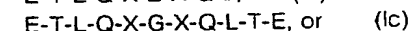
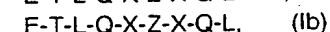
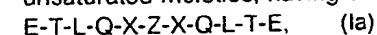
where na is 5 to 100, z is 1 to 10 and Y is a direct bond when La is divalent or hydrogen when La is monovalent, and A, R, m and n are as hereinbefore defined.

More specifically the macromer is as seen in formulas Ia to Id,



wherein all the variables are as hereinbefore defined.

The instant invention further provides a crosslinked polymer which is the addition polymerization product of (a) a macromer containing perfluoropolyalkylether and polyalkylether segments and ethylenically unsaturated moieties, having the formula I, more specifically as seen in formulas Ia to Id,



as hereinbefore defined, and

b) a vinylic comonomer which is

(i) a hydrophilic vinylic monomer,

(ii) a hydrophobic vinylic monomer,

(iii) a polyreactive crosslinking agent,
or (iv) a mixture of one or more (i), (ii) and (iii).

Preferably the macromer is of formula Ia.

In the foregoing perfluoropolyether portion Z of the macromer, a is preferably 1 or 2, and b is preferably 3 to 50. The definition of Z comprises block structures as well as alternating structures relating to different sub-groups having the index a. X is preferably $-\text{CH}_2-$ or $-\text{CH}_2(\text{OCH}_2\text{CH}_2)_y-$ where y is 1 or 2. A is preferably oxa.

Q is preferably $-\text{OCONH-R-NHCO}-$ where R is a radical derived from diisocyanates including hexane-1,6-diisocyanate, trimethyl-hexane-1,6-diisocyanate, tetramethylene-diisocyanate, phenylene-1,4-diisocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, m- and p-tetramethylxylenediisocyanate, isophorone-diisocyanate and cyclohexane-1,4-diisocyanate, and most preferably isophorone-diisocyanate, from which both NCO-Groups have been abstracted.

L is preferably a polyalkylether, $-\text{O}(\text{C}_m\text{H}_{2m}\text{O})_n\text{C}_m\text{H}_{2m}\text{O}-$ where m is 2 or a mixture of 2 and 3, more preferably m is 2 and n is 10-50. Where m is a mixture of 2 and 3, the mixture contains a major proportion of subgroups where m is 2.

T is preferably $-\text{CONH-R}_5\text{A}-$ where R_5 is preferably ethylene and A is preferably oxa. Where T is $-\text{CONH-R-NHCOOR}_5\text{A}-$, R is preferably a radical derived from isophorone diisocyanate and R_5 is preferably ethylene.

E is preferably $-\text{CO-C}(\text{R}_1)=\text{CHR}_2$ where R_1 is preferably methyl and R_2 is preferably hydrogen. Where E is $-\text{CONH-phenyl-C}(\text{R}_1)=\text{CHR}_2$, R_1 and R_2 are preferably hydrogen. Where E is $-\text{CONH-C}(\text{R}_4)_2\text{-phenyl-C}(\text{R}_1)=\text{CHR}_2$, R_1 is preferably methyl and R_2 is hydrogen.

Where G is present, x is preferably 1, and R is preferably a radical derived from isophorone diisocyanate.

Where La is present, A is preferably oxa, R is preferably a radical derived from isophorone diisocyanate, z is preferably 1 to 5 and preferably n equals na.

Preferred is a macromer of formula Ia wherein

E is $-\text{CO-C}(\text{CH}_3)=\text{CH}_2$,

T is $-\text{CONH-CH}_2\text{CH}_2\text{-O}-$,

L is $-\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{C}_2\text{H}_4\text{O}-$ where n is 19-25,

Q is $-\text{OCONH-isophorone-NHCO}-$,

X is $-\text{CH}_2-$, and

Z is $-\text{CF}_2\text{O}(\text{C}_2\text{F}_4\text{O})_r-(\text{CF}_2\text{O})_s-\text{CF}_2$ where

r:s is in the range of 1:10 to 5:1 and is preferably about 0.7.

The invention is further directed to a crosslinked homopolymerization product of a macromer E-T-L-Q-X-Z-X-Q-L-T-E or E-T-L-Q-X-G-X-Q-L-T-E wherein the variables are as hereinbefore defined. The invention is also directed to a crosslinked copolymerization product of the macromer E-T-L-Q-X-Z-X-Q-L-T-E and E-T-L-Q-X-Z-X-Q-L wherein the variables are as hereinbefore defined.

A further embodiment of the invention is a crosslinked homopolymerization product of a macromer E-T-L-Q-X-Z-X-Q-L-T-E wherein

E is $-\text{CO-C}(\text{CH}_3)=\text{CH}_2$,

T is $-\text{CONH-CH}_2\text{CH}_2\text{-O}-$,

L is $-\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{C}_2\text{H}_4\text{O}-$ where n is 19-25,

Q is $-\text{OCONH-isophorone-NHCO}-$,

X is $-\text{CH}_2-$, and

Z is $-\text{CF}_2\text{O}(\text{C}_2\text{F}_4\text{O})_r-(\text{CF}_2\text{O})_s-\text{CF}_2$ where

r:s is in the range of 1:10 to 5:1 and is preferably about 0.7.

In the crosslinked copolymerization product of a macromer E-T-L-Q-X-Z-X-Q-L-T-E and E-T-L-Q-X-Z-X-Q-L preferably greater than 1 % of the material is derived from the macromer E-T-L-Q-X-Z-X-Q-L-T-E, more preferably greater than 10 %, more preferred greater than 20 % and advantageously greater than 30 %.

This invention is further directed to an ophthalmic device made of the homopolymerization or copolymerization products mentioned hereinbefore, especially to contact lenses made therefrom. These contact lenses are preferably hydrogel contact lenses having greater than 20 % water content, more preferably greater than 30 %, even more preferred greater than 40 %, advantageously greater than 50 % water content. A preferred range of hydrogel water content is about 25 to about 50 % water content in its equilibrated state.

The vinylic macromonomers of formula I can be prepared by methods known, per se.

For example, the perfluoropolyalkylether/polyalkylether containing divinyllic macromonomers of formula Ia can be prepared in a three-step sequential synthesis. In the first step, a perfluoropolyalkylether dialkanol

of the formula $\text{HOCH}_2(\text{C}_a\text{F}_{2a}\text{O})_b(\text{CF}_2)\text{-CH}_2\text{OH}$ is reacted with two moles of a difunctional reactive agent, e.g. a diisocyanate of the formula OCN-R-NCO in the presence of a urethane catalyst to form the corresponding reactive group containing endcapped derivative $\text{Z}_1\{\text{NCO}\}_2$, where Z_1 is a moiety containing a perfluoropolyalkylether segment. In the second step, the resulting endcapped perfluoropolyalkylether derivative $\text{Z}_1\{\text{NCO}\}_2$ can then be reacted with two moles of a polyoxyalkylene diol of the formula $\text{HO-}(\text{C}_m\text{H}_{2m}\text{O})_{n+1}\text{-H}$ preferably in the presence of a conventional aprotic solvent at a temperature between about -10°C to about 100°C , to form the corresponding polyalkylether-perfluoropolyalkylether-polyalkylether derivative of the formula $\text{Z}_1\{\text{-NH-C(O)-O-(C}_m\text{H}_{2m}\text{O)}_{n+1}\text{-H}\}_2$. In the third step, this triblock diol can be then reacted with two moles of reactive group containing vinylic monomer, wherein the reactive group is an isocyanate, say, of the formula $\text{O=C=N-(R-NHCOO)}_t\text{R}_5\text{A-C(O)CR}_1=\text{CHR}_2$ wherein R, A, R_1 , R_2 and R_5 are as above defined and t is 0 or 1, at a temperature between about -10°C to about 100°C in the presence of a conventional aprotic solvent, in the further presence or absence of a catalytic amount of urethane catalyst.

Materials comprising polymers of the formulas Ib and Id are formed by partial (or incomplete) capping in a reaction step. These materials are useful where post-polymerization modifications are performed such as tinting with reactive dyes.

Suitable aprotic solvents for conducting the reactions include formamide, N,N-dimethylformamide, phosphoric acid tri-dimethylamide, N-methyl-2-pyrrolidone, N,N-dimethylacetamide, acetamide, acetonitrile, acetone, tert-butyl acetate and preferably isopropyl acetate.

Suitable urethane catalysts include tertiary amines such as trimethylamine, triethylamine, N,N-dimethylbenzylamine, or an organo-metallic urethane catalyst, such as stannous octoate or dibutyltin dilaurate, or sodium acetate.

Alternatively the difunctional reactive agent can be an activated carboxy, such as anhydride, an acid halide, a carboxy ester or oxirane, or is a leaving group, such as halide, sulfato or the like. It is clear that reactants in the various steps of the synthesis be coreactive, e.g. if the perfluoropolyalkylether is terminated with an amine group, the reactive agent can contain an isocyanate, ester, acid halide, halide and the like. These coupling reactions are well known in the art.

The perfluoropolyalkylether starting materials are known and some are commercially available. They are described in U.S. Patent Numbers 3,810,874, 3,810,875, 3,847,978, 4,085,137, 4,094,911, 4,089,319 and 4,440,918 and European Patent Applications 084406 and 211237 and Japanese Patent Applications cited hereinbefore. Perfluoropolyalkylether dimethanols can be prepared by photooxidation of tetrafluoroethylene followed by cleavage and reduction reactions. Some of these are available from Ausimont, USA and are known as Fomblin ZDOL derivatives such as Fomblin ZDOL 2000, Fomblin ZDEAL 2000 and Fomblin Z-DISOC with the respective formulas being $\text{Z}\{\text{CH}_2\text{OH}\}_2$, $\text{Z}\{\text{COOCH}_3\}_2$, $\text{Z}\{\text{CONH-C}_6\text{H}_3(\text{CH}_3)\text{NCO}\}_2$ where Z is $\text{CF}_2\text{O}(\text{C}_2\text{F}_4\text{O})_r\text{-(CF}_2\text{O)}_s\text{-CF}_2$ (r/s ~ 0.7). One can also chain extend these materials, for example the diols with diisocyanates, before use (see definition of G).

Difunctional (or multifunctional) reactive materials such as diisocyanate, diester, diepoxides and so on are known and many are commercially available.

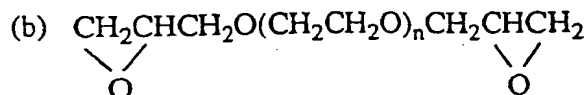
The polyalkylether starting materials are also well known and many are commercially available (e.g. from Aldrich, Olin and Polysciences). Hydroxy terminated polyethylene glycols, average molecular weights 200-10,000 are available from Aldrich Chemical Company, Inc. USA. Amine-terminated polyethylene glycols are known and some are commercially available, for example, Jeffamine D-400 (Jefferson Chemical and Texaco).

It is also possible to use polyalkylether copolymers such as ethylene/propylene oxide polymeric diols where the more hydrophilic ethylene oxide is in major proportion. Many polymeric copolymeric diols are known and are described in U.S. Patent No. 4,780,488. These copolymers include poloxamers which are sold under the trade name Pluronic (BASF Wyandotte). One can also chain-extend the diols with, for example, diisocyanates before use (see definition of La).

In the third step of the reaction, the reactive vinylic group is introduced. Isocyanate terminated vinylic monomers are known and some are described in U.S. Patent No. 4,665,123. Some are commercially available such as 2-isocyanatoethyl methacrylate (Dow Corning, USA) and m-isopropenyl-2,2-dimethylbenzyl-isocyanate (m-TMI, Cyanamid). Epoxy terminated vinylic monomers, e.g. glycidyl methacrylate, are known and are commercially available.

It is also within the scope of the invention to prepare a macromer of formula I by endcapping

(a) $\text{HOCH}_2(\text{C}_a\text{F}_{2a}\text{O})_b\text{-CF}_2\text{-CH}_2\text{OH}$ where a is 1 to 4 and b is 2 to 200 with



where n is 5 to 100 followed by reaction with

(c) 2-isocyanatoethyl methacrylate wherein the reactants a:b:c are in a 1:2:2 molar ratio.

The invention is further directed to a crosslinked homopolymerization product of such macromer, to an ophthalmic device therefrom, especially a contact lens made therefrom.

It is useful to add minor amounts i.e. up to about 10 % of vinylic comonomer to the composition, for example, to enhance tintability of the materials. These vinylic comonomers contain reactive groups such as hydroxyl, amine, oxirane and so forth. It is also useful to fine tune a particular physical property such as modulus, elongation, tensile strength, hydrophilicity or oxygen permeability by adding minor amounts of additional comonomers.

The vinylic comonomer may be hydrophilic, hydrophobic or may be a mixture of hydrophilic and hydrophobic vinylic monomers. Suitable vinylic monomers include those conventional vinylic monomers generally employed in the fabrication of soft and hard contact lenses. By a hydrophilic vinylic monomer is meant a monomer which, when polymerized by conventional free radical polymerization, characteristically yields a polymer which either dissolves in water or is capable of absorbing at least 10 % by weight water under ambient equilibrium conditions. Similarly, suitable hydrophobic vinylic monomers are those monomers which, when polymerized by conventional free radical polymerization, characteristically yield a polymer which neither dissolves in water, nor is capable of absorbing at least 10 % by weight water under ambient (i.e. 20 °C) equilibrium conditions.

The derivatives of formula I, in the absence or presence of vinylic comonomer, are advantageously polymerized in the presence of an inert diluent or solvent, such as a suitable organic solvent, including a lower alkanol, e.g. ethanol, methanol or the like, or an aprotic solvent such as N,N-dimethylformamide, acetamide, acetonitrile, N,N-dimethylacetamide, dimethyl sulfoxide, acetone, tert-butyl acetate, isopropyl acetate or mixture thereof. Also, aqueous/organic solvent systems may be employed.

The derivatives of formula I, in the absence or presence of a vinylic comonomer are polymerized in the presence of actinic radiation or in the presence of a conventional free radical initiator, such as a peroxide, e.g. di-tert-butyl peroxide, benzoyl peroxide, lauryl peroxide, decanoyl peroxide, acetyl peroxide, succinic acid peroxide, methyl ethyl ketone peroxide, 2,4-dichlorobenzoyl peroxide, isopropyl peroctoate, tert-butyl hydroperoxide, tert-butyl perpivalate, tert-butyl peroctoate, diisopropyl peroxydicarbonate, cumene hydroperoxide, tert-butyl perbenzoate, tert-butyl peroxy maleic acid, tert-butyl peroxyacetate, and potassium persulfate, an azo compound, e.g. 2,2-azo-bis-isobutyronitrile, 2,2'-azo-bis-(2,4-dimethylvaleronitrile), 1,1'-azo-bis-(cyclohexane carbonitrile), 2,2'-azo-bis-(2,4-dimethyl-4-methoxyvaleronitrile) and phenyl-azo-isobutyronitrile, a photoinitiator, e.g. benzoin methyl ether and 1-hydroxycyclohexylphenyl ketone or actinic radiation such as UV light or ionizing rays e.g. gamma rays or X-rays.

The derivatives of formula I, in the absence or presence of a vinyl comonomer, are advantageously polymerized upon placement into a mold. The mold may be a conventional spin-casting mold for preparing contact lenses such as described in U.S. Patent No. 3,408,429, or a static mold, e.g. as described in U.S. Patent No. 4,347,198. Alternately, one may prepare a swollen lens blank, dry the lens blank to form the corresponding xerogel, shape the xerogel into a contact lens precursor by lathing methods known to the art, and swell the shaped xerogel in aqueous medium to form the corresponding contact lens, as described in Reissue U.S. Patent No. 27,401.

The solution of derivatives of formula I, in the absence or presence of a vinylic comonomer, is advantageously placed into a mold in the shape of a contact lens and polymerized. After polymerization, the crosslinked polymer is equilibrated in aqueous or aqueous saline solution. Optimally this post treatment further includes a heat treatment of the molded lens shaped polymer. Such heat treatment is characteristically conducted at a temperature between about 60 and 100 °C, e.g. in the presence of an aqueous medium. The treatment can vary greatly, but usually is accomplished in about 5 to 90 minutes. The purpose of this post treatment is to dimensionally stabilize the crosslinked contact lens material. Also, the treatment may further serve to sterilize such lens material.

Suitable vinylic comonomers for polymerization with the derivative of formula I include conventional hydrophobic and hydrophilic monomers. Suitable hydrophobic monomers include, without limitation, C₁ to C₁₈ alkyl acrylates and methacrylates, C₃ to C₁₈ alkyl acrylamides and methacrylamides, acrylonitrile, methacrylonitrile, vinyl C₁ to C₁₈ alkanoates, C₂ to C₁₈ alkenes, C₂ to C₁₈ haloalkenes, styrene, C₁ to C₆ alkyl styrenes, vinyl alkyl ethers wherein the alkyl portion has 1 to 6 carbon atoms, C₃-C₁₂ perfluoroalkyl

ethyl thiocarbonylaminoethyl acrylates and methacrylates, C₃-C₁₂ fluoroalkyl acrylates and methacrylates, acryloxy and methacryloxy-alkyl-siloxanes, N-vinylcarbazole, C₁-C₁₂ alkyl esters of maleic, fumaric, itaconic, and mesaconic acids and the like. Examples of suitable hydrophobic monomers include methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, styrene, chloroprene, vinyl chloride, vinylidene chloride, acrylonitrile, 1-butene, butadiene, methacrylonitrile, vinyl toluene, vinyl ethyl ether, perfluorohexylethylthiocarbonylaminoethyl methacrylate, isobornyl methacrylate, hexafluorobutyl methacrylate, 3-methacryloxypropylpentamethyldisiloxane, and bis-(methacryloxypropyl) tetramethyldisiloxane.

Suitable hydrophilic monomers include, without limitation, hydroxy substituted lower alkyl acrylates and methacrylates, acrylamide, methacrylamide, C₁-C₂ lower alkyl acrylamide and methacrylamide, ethoxylated acrylates and methacrylates, hydroxy substituted lower alkyl acrylamide and methacrylamide, hydroxy substituted lower alkyl vinyl ethers, sodium ethylene sulfonate, sodium styrenesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, N-vinylpyrrole, N-vinylsuccinimide, N-vinylpyrrolidone, 2- and 4-vinylpyridine, acrylic acid, methacrylic acid, amino (by amino including quaternary ammonium), -monolower-alkylamino- or diloweralkylamino-lower alkyl acrylates or methacrylates, allyl alcohol, and the like.

Specific hydrophilic monomers include hydroxyethyl methacrylate, hydroxyethyl acrylate, acrylamide, methacrylamide, N,N-dimethylacrylamide, allyl alcohol, vinylpyridine, N-vinylpyrrolidone, glycerol methacrylate, N(1,1-dimethyl-3-oxobutyl) acrylamide, and the like.

Preferred hydrophobic comonomers are methyl methacrylate and glycidyl methacrylate.

Preferred hydrophilic monomers are 2-hydroxyethyl methacrylate, N-vinyl pyrrolidone, and dimethylacrylamide.

Optionally, an additional conventional polyreactive crosslinking agent may be added, such as, allyl compounds e.g. allyl methacrylate, diallyl itaconate, monoallyl itaconate, diallyl fumarate, diallyl succinate, diallyl phthalate, triallyl cyanurate, triallyl isocyanurate, diethylene glycol bis-allyl carbonate, triallyl phosphate, triallyl trimellitate, allyl ether, N,N-diallylmelamine; vinyl compounds, e.g. divinyl benzene, N,N'-methylene-bis acrylamide, ethylene glycol dimethacrylate, neopentylglycol dimethacrylate, tetraethylene glycol dimethacrylate, hexamethylene-bis-maleimide, divinyl urea, bisphenol A bis methacrylate, divinyl adipate, glycerin trimethacrylate, trimethylolpropane triacrylate, trivinyl trimellitate, 1,5-pentadiene, 1,3-bis(4-methacryloxybutyl) tetramethyl disiloxane, divinyl ether and divinyl sulfone; hydroxyl reactive compounds such as: polyvalent isocyanates e.g. hexamethylene diisocyanate, isophorone diisocyanate, toluene diisocyanate; polyaldehydes e.g. glutaraldehyde and glyoxal; polyacids e.g. glutaric acid and oxalic acid; polyepoxides e.g. butane diepoxide, vinylcyclohexene dioxide and butanediol diglycidyl ether; polyols (acid catalysis) e.g. dimethylol urea and diethylene glycol. Also the dimethacrylate formed by reacting perfluoropolyalkylether dimethanol or poly(ethylene glycol) with two moles of isocyanatoethyl methacrylate can be used.

When employed, about 0.01 to 10 weight percent of crosslinking agent, based upon the weight of formula I derivative, may be present, preferably about 0.01 to about 5 percent, most preferably about less than 2 weight percent.

The resultant contact lenses are optically clear, strong, flexible, highly oxygen permeable and wettable. Further, the instant lenses are characterized by their ease of manufacture.

In the following examples, all parts are by weight unless otherwise described.

A description of testing methods used on the polymer films is as follows: Oxygen permeability (DK) is determined from measurements on a Schema Versatae or Createch polarographic cell. Wettability or lubricity is evaluated by a feel comparison to crosslinked polyHEMA (i.e. polymerized 2-hydroxyethyl methacrylate + 1 % ethylene glycol dimethacrylate). The surface lubricity of polyHEMA is designated (B); more wettable than polyHEMA is designated (A) and a less wettable surface than polyHEMA is designated (C). Tensile strength is qualitatively evaluated by pulling on a sheet of the material by hand and then comparing the result to a material previously evaluated by a micromechanical tester to be 14 kg/cm². A measurement found to be similar to this "standard" is designated (2); a higher value is designated (1); a lower value is designated (3); while a much lower value is designated (4).

Example 1:

This example illustrates the sequential synthesis of the perfluoropolyether/polyether urethane-linked adduct, Z₁-(IPDI-PEG-IEM)₂, where Z₁ is a perfluoropolyether, IPDI is isophorone diisocyanate, PEG is a polyethylene glycol and IEM is 2-isocyanatoethyl methacrylate; and the solution polymerization of this

adduct.

Synthesis of $Z_1-(IPDI-PEG)_2$ Diadduct:

30.06 g (0.0136 mole) Fomblin ZDOL 2000 (MW 2200; Montedison, Ausimont) is combined with 6.07 g (0.02734 mole) IPDI and 10 μ l dibutyltin dilaurate, mixed well and stirred overnight at room temperature forming $Z_1-(IPDI)_2$. The percentage of isocyanate reacted (generally 48-54 %) is determined by dibutylamine titration and varies with the precise value of the Z_1 molecular weight actually used. Then, the calculated molar amount of PEG is added to a solution (solvent, 30-70 %) of $Z_1-(IPDI)_2$ to form $Z_1-(IPDI-PEG)_2$. Then a urethane catalyst, i.e. dibutyltin dilaurate (0.66 ml per gram of solute) is added and the solution allowed to react at 50 °C with stirring overnight (complete disappearance of isocyanate IR absorption at 2270 cm^{-1}).

Synthesis of $Z_1-(IPDI-PEG-IEM)_2$ Diadduct:

The calculated molar amount of IEM is added, with rapid stirring, to a solution of $Z_1-(IPDI-PEG)_2$ and reacted at 40-50 °C (see example 2 samples 1-3) or at room temperature (see example 2 sample 5 and 6).

Polymerization of Diadduct: Hydrogel Formation:

The $Z_1-(IPDI-PEG-IEM)_2$ adduct in a solvent is mixed with initiator (benzoin methyl ether, BME), poured into flat "sandwich" molds and polymerized with UV light (Sylvania, Blacklight Blue, 15 W) at room temperature for 3 hours. The polymerized films are removed from the molds, extracted in water several times, heated in boiling water for 10 minutes and then allowed to equilibrate in room temperature water (generally overnight).

Example 2:

This example shows the resultant water content and oxygen permeability values of perfluoropolyalkylether/PEG hydrogels, i.e. crosslinked $Z_1-(IPDI-PEG-IEM)_2$, solution polymerized using different molecular weights of PEG (400,600) in various amounts of solvent (acetone).

Wt. % In the Polymerization Mixture							Wt.% BME	% H ₂ O Content	DK (barrer)
Sample	Z ₁	IPDI	PEG	(MW)	IEM	Acetone			
1	39.2	7.9	14.3	(400)	5.5	33.0	0.1	14.5	67.0
2	20.3	4.1	7.4	(400)	2.9	65.3	0.2	28.9	68.4
3	34.7	7.1	19.0	(600)	4.9	34.3	0.04	29.2	46.2
4	31.6	6.4	17.4	(600)	4.5	40.1	0.3	37.3	51.6
5	26.0	5.3	14.3	(600)	3.7	50.8	0.3	36.9	53.0
6	16.1	3.3	8.9	(600)	2.3	69.5	0.4	49.2	51.5

As shown above, water content increases with higher molecular weight PEG and reaction solvent content. The oxygen permeability, however, decreases with the higher molecular weight PEG.

Example 3:

This example illustrates a range of Z_1 /PEG hydrogel water contents obtained by varying the molecular weight of the PEG and the proportion of solvent IPAC (isopropyl acetate). Films are made as in example 1 except that the molecular weight of the PEG is 600, 900, 1000 or 1500 and the solvent used is isopropyl

acetate. IEM is reacted at 40-50 ° C for all samples.

Sample	Wt.% In the Polymerization Mixture						Wt.% BME	% H ₂ O Content
	Z ₁	IPDI	PEG	(MW)	IEM	IPAC		
1	35.3	7.2	19.3	(600)	5.0	33.2	0.06	21.9
2	27.1	5.5	14.8	(600)	3.8	48.8	0.06	31.2
3	20.8	4.2	11.3	(600)	2.9	60.8	0.04	45.8
4	29.4	5.9	24.0	(900)	4.1	36.6	0.05	39.5
5	25.2	5.1	20.6	(900)	3.6	45.7	0.04	40.7
6	20.9	4.2	17.1	(900)	3.0	54.8	0.05	42.8
7	27.3	5.5	24.9	(1000)	3.9	38.4	0.05	42.9
8	23.8	4.8	21.7	(1000)	3.4	46.3	0.05	45.1
9	22.0	4.4	20.0	(1000)	3.3	47.7	0.05	45.0
10	20.2	4.1	18.3	(1000)	2.8	54.6	0.03	48.1
11	15.9	3.2	14.5	(1000)	2.2	64.2	0.05	54.2
12	13.9	2.8	12.6	(1000)	2.0	68.7	0.04	52.9
13	18.9	3.9	25.9	(1500)	2.7	48.6	0.05	57.9
14	16.5	3.4	22.6	(1500)	2.3	55.2	0.06	61.1
15	14.7	3.1	20.1	(1500)	2.1	60.1	0.07	61.5

As shown above water content increases with increasing molecular weight PEG and solvent content.

Example 4:

This example shows the effect of hydrophilic comonomer addition on the physical properties of Z₁/PEG hydrogel films. Films are made as in example 3 except that the comonomer N,N-dimethylacrylamide (DMA), N-vinylpyrrolidone (NVP) or 2-hydroxyethyl methacrylate (HEMA) is added just prior to the addition of initiator.

Sample	Wt.% In the Polymerization Mixture							% BME
	Z ₁	IPDI	PEG	(MW)	IEM	Comonomer	IPAC	
1	24.4	4.9	19.9	(900)	3.4	17.1 DMA	30.3	0.05
2	24.5	4.9	20.0	(900)	3.5	16.7 NVP	30.4	0.05
3	24.5	4.9	20.0	(900)	3.5	16.6 HEMA	30.5	0.05
4	29.4	5.9	24.0	(900)	4.1	-	36.6	0.05
5	24.8	5.0	22.6	(1000)	3.5	9.1 DMA	35.0	0.05
6	22.8	4.6	20.7	(1000)	3.2	16.6 DMA	32.1	0.05
7	21.0	4.3	19.1	(1000)	3.0	9.5 DMA	43.1	0.06
8	19.2	3.9	17.5	(1000)	2.7	17.4 DMA	39.4	0.05
9	24.8	5.0	22.6	(1000)	3.5	9.2 NVP	34.9	0.05
10	22.7	4.6	20.7	(1000)	3.2	16.8 NVP	32.0	0.05
11	21.1	4.3	19.2	(1000)	3.0	9.0 NVP	43.4	0.04
12	19.2	3.9	17.4	(1000)	2.7	17.5 NVP	39.3	0.05
13	24.8	5.0	22.6	(1000)	3.5	9.1 HEMA	35.0	0.05
14	22.8	4.6	20.7	(1000)	3.2	16.6 HEMA	32.1	0.05
15	21.0	4.2	19.0	(1000)	3.0	9.8 HEMA	43.0	0.05
16	19.2	3.9	17.5	(1000)	2.7	17.4 HEMA	39.4	0.05
17	27.3	5.5	24.9	(1000)	3.9	-	38.4	0.05
18	15.7	3.3	21.5	(1500)	2.2	16.8 DMA	40.5	0.05
19	15.7	3.3	21.5	(1500)	2.2	16.8 NVP	40.5	0.05
20	15.4	3.2	21.5	(1500)	2.2	18.9 HEMA	39.8	0.06
21	18.9	3.9	25.9	(1500)	2.7	-	48.6	0.05

Physical Properties of Hydrogel				
Sample	% H ₂ O Content	Clarity	Wettability	Strength
1	54.4	Clear	A	3
2	48.8	Clear	A	3
3	37.1	Clear	A	2
4	39.5	Clear	A	2
5	52.6	Clear	A	3
6	57.1	Clear	A	3
7	54.4	Clear	A	3
8	60.1	Clear	A	3-4
9	48.6	Clear	A	3
10	54.7	Hazy	A	4
11	49.7	Clear	A	3
12	52.3	Clear	A	4
13	42.7	Clear	A	3
14	40.0	Clear	A	3
15	44.9	Sl. Hazy	A	3
16	44.8	Sl. Hazy	A	3
17	42.9	Clear	A	3
18	69.6	Clear	A	3
19	63.2	Clear	A	3-4
20	55.8	Hazy	A	2
21	57.9	Clear	A	3

As shown above, addition of hydrophilic comonomers has little effect on wettability or tensile strength.

Example 5:

This example compares the effect of initiator level on the physical properties of similar composition Z_1 /PEG hydrogel films. The films are prepared in a similar manner to that in example 1.

In general, 3.00 g (0.0016 mole) Fomblin ZDOL 2000, MW 1851 (previously bubbled with nitrogen for 2 hours while stored over molecular sieves) is combined with 0.72 g (0.0032 mole) IPDI and 2.5 μ l dibutyltin dilaurate (DBTL) catalyst under nitrogen, mixed well and stirred overnight at room temperature. The percentage of isocyanate reacted is determined by titration to be 48-53 %. PEG 1000 is reacted with $Z_1-(IPDI)_2$ in the presence of solvent (approximately 38 % by weight isopropyl acetate, IPAC). Then 0.66 μ l DBTL is added per gram solute and the solution reacted at 50 °C with stirring overnight under nitrogen. The calculated equimolar amount of IEM is added, with rapid stirring, to a solution of $Z_1-(IPDI-PEG)_2$. The solution is cooled to room temperature and initiator (BME) added. The solution is centrifuged five minutes (Eppendorf 5412) poured into "sandwich" molds and UV irradiated at room temperature for three hours. After water extraction, strength and wettability testing is performed.

Sample	Wt. % In the Polymerization Mixture						Hydrogel % H ₂ O Content
	Z ₁	IPDI	PEG	IEM	IPAC	% BME	
1	24.8	5.9	26.8	4.2	38.4	0.05	36.7
2	24.6	5.9	26.7	4.2	38.7	0.05	47.9
3	25.9	5.8	25.9	4.0	38.4	0.1	46.3
4	24.8	6.0	26.8	4.1	38.3	0.1	47.5
5	24.7	6.0	26.8	4.2	38.4	0.1	50.4
6	25.9	5.8	25.9	4.0	38.4	0.2	48.4
7	24.8	6.0	26.8	4.1	38.3	0.2	51.3
8	25.9	5.8	25.9	4.0	38.4	0.5	48.8

All hydrogels are clear. The wettability is (A) for samples 2, 4, 5, 7 and 8 and (B) for samples 1,3 and 6. The strength is (2) for samples 1, 3, 6 and 8, (3) for samples 4, 5 and 7 and (4) for sample 2. As shown above, increasing initiator level from 0.05 to 0.1 % and higher appears to improve property reproducibility especially water content and strength; but no added strength is found by further increasing initiator level to 0.5 %

Example 6:

This example illustrates the effect of various crosslinking agents on the physical properties of perfluoropolyether/PEG hydrogel films. The crosslinkers used are: a dimethacrylate of PEG 600, a dimethacrylate of ZDOL 1000 and ethylene glycol dimethacrylate.

The dimethacrylate of PEG 600 is synthesized by combining 2.425 g (0.004 mole) PEG 600 with 1.2578 g (0.008 mole) IEM, mixing well and adding 2 μ l DBTL and stirring overnight at room temperature. Reaction completion is indicated by disappearance of isocyanate IR absorption at 2270 cm^{-1} .

The dimethacrylate of ZDOL 1000, $Z_1-(IEM)_2$, is synthesized by combining 1.1115 g (0.00085 mole) Fomblin ZDOL 1000 (MW 1301) with 0.2652 g (0.0017 mole) IEM, mixing well and then adding 2 μ l DBTL and stirring for three hours at room temperature. Disappearance of the isocyanate IR absorption is used to monitor reaction completion. Ethylene glycol dimethacrylate (EGDMA) is distilled from a commercial source (Sartomer) before use.

Wt.% In the Polymerization Mixture								
Sample	Z ₁	IPDI	PEG 1000	IEM	IPAC	Comonomer	% BME	Hydrogel % H ₂ O Content
1	22.4	5.4	24.3	3.8	34.8	9.3 PEG 600(IEM) ₂	0.1	49.8
2	19.9	4.8	22.4	3.5	36.2	13.1 PEG 600(IEM) ₂	0.1	48.3
3	20.7	4.9	22.3	3.5	35.4	13.2 PEG 600(IEM) ₂	0.09	48.6
4	24.4	5.9	26.4	4.1	38.1	1.1 EGDMA	0.1	45.3
5	24.5	5.9	26.4	4.1	38.1	1.0 ZDOL 1000(IEM) ₂	0.1	53.6
6	24.7	5.9	26.7	4.2	38.5	1.0 ZDOL 1000(IEM) ₂	0.1	46.7
PEG 600(IEM) ₂ = PEG 600 terminated with 2 equ. IEM EGDMA = ethylene glycol dimethacrylate; ZDOL 1000(IEM) ₂ = ZDOL 1000 terminated with 2 equ. IEM as described in this example.								

All hydrogels are clear. The wettability is (B) for sample 4 and (A) for the remaining samples. The strength is (2-3) for sample 5, (3) for samples 1, 4 and 6 and (4) for samples 2 and 3.

Example 7:

This example shows the physical properties of perfluoropolyether/PEG hydrogel films made by combining the diadducts of Z₁-(IPDI-PEG-IEM)₂ which have different PEGs, but the same Z₁ (i.e. ZDOL 2000). The PEGs used are 400, 600 and 1000.

The reaction solutions are prepared in isopropyl acetate as in example 5 except that nitrogen degassing is not used. The solutions are mixed in various ratios just prior to initiator (BME) addition.

Wt. % In the Polymerization Mixtures								
Mole Ratio								Hydrogel % H ₂ O Content
Sample	Z ₁ -(IPDI-PEG-IEM) ₂	Z ₁	IPDI	PEG (MW)	IEM	IPAC	% BME	
1	1 PEG 1000/1 PEG 600	27.1	6.5	14.8(1000) 8.7(600)	4.6	38.3	0.05	39.0
2	3 PEG 1000/1 PEG 600	25.9	6.2	21.1(1000) 4.1(600)	4.3	38.4	0.06	42.4
3	1 PEG 1000/1 PEG 400	28.6	6.5	15.6(1000) 6.1(400)	4.8	38.3	0.05	35.0
4	3 PEG 1000/1 PEG 400	26.5	6.4	21.2(1000) 2.9(400)	4.5	38.3	0.05	40.9
5	PEG 1000	24.7	5.9	26.7(1000)	4.2	38.5	0.1	46.7
All hydrogels are clear, have an (A) wettability and a (3) strength.								

The results show that though the water content of a Z₁-(IPDI-PEG 1000-IEM)₂ film is lowered slightly by the copolymerization with Z₁-(IPDI-PEG 400-IEM)₂ or Z₁-(IPDI-PEG 600-IEM)₂, the clarity, wettability and strength appear the same.

Example 8:

This example shows the effect of a lower molecular weight (i.e. approximately 1000 as opposed to approximately 2000) perfluoropolyether on the properties of a Z₁/PEG hydrogel. The synthesis of these

$Z_1-(IPDI-PEG-IEM)_2$ diadducts is similar to that described in example 3. More specifically, 5.0082 g (0.0038 mole) Fomblin ZDOL 1000 (MW 1301) is reacted with 1.7121 g (0.0077 mole) IPDI in solvent (20 % isopropyl acetate) while stirring at room temperature overnight in the presence of 2 μ l DBTL; some samples (i.e. sample numbers 3, 5 and 6) are reacted without solvent. The $Z_1-(IPDI)_2$ diadduct is then reacted with 2 moles of PEG (i.e. 200, 400, 600, 900 or 1000). The PEG is first dissolved in a certain quantity of isopropyl acetate (the weight of solvent calculated to be 40 % of the final reaction mixture) at 50 °C (PEG 600, 900, 1000) or at room temperature (PEG 200, 400).

In sample 1 for example, 0.2211 g (0.0011 mole) PEG 200 is dissolved in 0.5692 g IPAC then 1.2098 g of the $Z_1-(IPDI)_2$ adduct is added, the mixture mixed well followed by the addition of 0.78 μ l DBTL and stirring overnight at 50 °C. The solution is then cooled to room temperature, 0.1714 g (0.0011 mole) IEM added and the mixture reacted with stirring at room temperature overnight. Addition of initiator (BME), polymerization and water equilibration are similar to that described in example 1.

Sample	MW PEG	% BME	% H ₂ O Content	Physical Properties of Hydrogel	
				Oxygen Permeability (barrer)	Observation
1	200	0.48	5.92	25.3	very slightly hazy on edges; wettability = B
2	400	0.49	19.48	24.0	clear; wettability = B
3	600	0.06	34.29	20.8	clear; yellow edges; wettability = A
4	900	0.51	47.66	25.9	clear; wettability = A
5	1000	0.07	50.28	22.9	clear; wettability = A
6	1000	0.48	51.50	-	clear; wettability = A

As shown above, water content and wettability increase with increasing molecular weight of PEG.

Example 9:

This example shows the effect of PEG molecular weight and solvent content (isopropyl acetate) on various physical properties of perfluoropolyether/polyether hydrogels obtained using Fomblin ZDOL TX 2000 (Z_1 TX, MW 2288) a perfluoropolyether with an additional 1 or 2 ethylene oxide units adducted to the terminal hydrogel groups of ZDOL 2000.

Films are made in a similar manner to those described in example 3. The reaction of Z_1 TX and two moles of IPDI is monitored by isocyanate titration and the percent isocyanate reacted is found to be approximately 50 % (47-52 %). The product, $Z_1TX(IPDI-PEG-IEM)_2$ is formed through the reaction of two moles of IEM with $Z_1TX(IPDI-PEG)_2$ adduct in IPAC at room temperature overnight.

As shown in the table below, in general, use of the perfluoropolyether Z_1 TX yields strong clear films whose percent water content increases with PEG molecular weight and solvent content.

% IPAC

In the

Physical Properties of Hydrogel

Poly-

merization % H₂O

Sample MW PEG Mixture Content Clarity/Wettability/Strength

1	400	28	16	Clear	A	2
2	400	39	17	Clear	B	1
3	400	48	21	Hazy	B	2
4	400	66	28	Cloudy	B	2
5	600	38	29	Clear	A	1
6	600	50	30	Sl. hazy	A	2
7	600	59	39	Hazy	B	3

% IPAC

In the

Physical Properties of Hydrogel

Poly-

merization % H₂O

Sample MW PEG Mixture Content Clarity/Wettability/Strength

8	900	29	39	Clear	A	4
9	900	40	40	Clear	A	1
10	900	50	43	Clear	A	1
11	900	58	47	Clear	A	1
12	1000	28	47	Clear	A	1
13	1000	38	42	Clear	A	1
14	1000	38	40	Clear	A	2
15	1000	49	43	Clear	A	1
16	1000	59	47	Sl. hazy	A	4
17	1500	39	55	Clear	A	2
18	1500	39	56	Clear	A	2
19	1500	49	57	Clear	A	2
20	1500	59	60	Clear	A	1

Example 10:

This example shows the synthesis of a perfluoropolyether/polyether hydrogel in which the urethane group linking the perfluoropolyether chain and polyether chain (reaction with IPDI) is replaced by an ether linkage; this is accomplished by using an epoxy-terminated PEG.

More specifically, 2.1091 g (0.00096 mole) Fomblin ZDOL 2000 (MW 2200) is reacted at 60 °C overnight with 0.7749 g (0.00194 mole) polyethylene glycol 400 diglycidyl ether (PEG 400, Polysciences), using 0.0167 g triethylamine catalyst. After 16 hours, the temperature of the mixture (opaque) is raised to 70 °C, 0.0220 g triethylamine added and the mixture stirred overnight leading to a clear, yellow, viscous product, $Z_1-(O-PEG\ 400)_2$. Then 0.5213 g (0.00017 mole) of $Z_1-(O-PEG\ 400)_2$ is combined with 1.8890 g dimethyl sulfoxide, DMSO, (Aldrich Gold Label, 99.9 %) and 0.0539 g (0.00035 mole) IEM which is added dropwise to the rapidly stirring mixture. The solution is reacted at room temperature approximately 72 hours. Then 0.0040 g BME is added and the solution poured into a "sandwich" mold and UV irradiated at room temperature for 13 hours resulting in a soft gel. This material after equilibration in water becomes a clear hydrogel film.

Example 11:

This example shows the fabrication of prototype perfluoropolyether/polyether lenses from polypropylene contact lens molds. The reaction solution is made as in example 5 (samples 3-5) using 0.1 BME as initiator. The solution is pipetted into the lens molds and UV cured for 3 hours. After water extraction and boiling, one obtains optically clear, strong lenses. Micromechanical tensile tests performed on the lenses yield the following properties: stress of 3.6 kg/cm², Young's modulus of 26 kg/cm² and a 13 % elongation.

Example 12:

This example illustrates the preparation of hydrogels obtained via polymerization of partially IEM capped $Z_1-(IPDI-PEG\ 1000)_2$ adduct (Z_1 Adduct). The incompletely capped adduct, i.e. mixtures of PEG-IPDI- Z_1 -IPDI-PEG-IEM and IEM-PEG-IPDI- Z_1 -IPDI-PEG-IEM, is prepared as in example 1 except that 50 %-90 % of the amount of IEM is added to partially react the PEG 1000 hydroxyl groups. The adducts are then polymerized with or without comonomer (DMA, HEMA, NVP) into sheets (samples 1-5) or lenses (samples 6-8) using UV irradiation (3 hours, 0.05 % BME initiator) and water equilibration. Sample 8 is control.

Sample	Polymerization Mixture			
	Z_1 :IPDI:PEG:IEM Molar Ratio	% Z_1 Adduct	% IPAC	% Comonomers
1	1:2:2:1	61.9	38.1	-
2	1:2:2:1	54.6	45.4	-
3	1:2:2:1	49.6	41.2	9.2 DMA
4	1:2:2:1	49.6	41.2	9.2 HEMA
5	1:2:2:1	49.7	41.2	9.1 NVP
6	1:2:2:1.5	66.3	33.7	-
7	1:2:2:1.8	61.1	38.9	-
8	1:2:2:2	61.6	38.4	-

This example illustrates the preparation and physical properties of the hydrogels obtained when various amounts of the Z_1 -(IPDI-PEG-IEM)₂ diadduct (Z₁ Diadduct) are copolymerized with the reaction product (RP Adduct) of Z_1 -(IPDI-PEG)₂ and an equal molar amount of IEM. The Z_1 -(IPDI-PEG-IEM)₂ diadduct is prepared as in example 1 using 37.4 % IPAC as solvent. The RP Adduct is also prepared as in example 1 with 38.1 % IPAC except that 50 % of the amount of IEM is added. These materials, i.e. Z₁ Diadduct and RP Adduct in IPAC are combined in various ratios and UV polymerized (3 hours, 0.05 % BME initiator) into sheets.

Sample	Polymerization Mixture		% H ₂ O Content of Hydrogel
	% RP Adduct	% Z ₁ Diadduct	
1	85.4	14.6	53.01
2	84.6	15.4	52.08
3	50.0	50.0	44.39
4	50.0	50.0	48.01
5	14.8	85.2	44.16
6	100.0	-	54.71
7	-	100.0	44.45

As shown above, water content tends to increase with increasing RP Adduct content.

This example illustrates the tensile strength of lenses polymerized from the $Z_1-(IPDI-PEG\ 1000-IEM)_2$ diadduct (Z_1 Diadduct) with or without additional comonomer adducts. The $Z_1-(IPDI-PEG\ 1000-IEM)_2$ diadduct is prepared as in example 1. The comonomers used are prepared by reaction of 1 mole Z_1 with one mole IEM (Z_1/IEM) or two moles IEM ($Z_1-(IEM)_2$) using dibutyltin dilaurate as catalyst. The diadduct in IPAC is combined with the additional comonomer adduct(s) and polymerized using UV irradiation (3 hours, 0.1 % BME initiator).

Sample	Polymerization Mixture			% H ₂ O Content of Hydrogel
	% Z ₁ Diadduct	% Comonomer Adduct	% IPAC	
1	61.0	1.0 (Z ₁ IEM) ₂	38.0	47.6
2	57.6	1.1 (Z ₁ IEM) ₂ 5.5 Z ₁ /IEM	35.8	44.3
3 (Control)	61.6	-	38.4	48.7

Sample	Physical Properties of Hydrogel		
	Young's Modulus (kg/cm ²)	Stress (kg/cm ²)	% Elongation
1	21 ± 4	3.0 ± 0.9	14 ± 3
2	22 ± 5	2.9 ± 0.4	13 ± 3
3	25 ± 5	4.0 ± 0.7	15 ± 2

Claims

1. A macromer containing perfluoropolyalkylether and polyalkylether segments and ethylenically unsaturated moieties, having the formula I, more specifically as seen in formulas Ia to Id,

E-T-L-Q-X-Z-X-Q-L-T-E, (Ia)

E-T-L-Q-X-Z-X-Q-L, (Ib)

E-T-L-Q-X-G-X-Q-L-T-E, (Ic)

E-T-L-Q-X-G-X-Q-L, (Id)

wherein

Z is $-(C_aF_{2a}O)_b-CF_2-$, where a is 1 to 4 or a mixture thereof and b is 2 to 200;

X is a direct bond, $-CH_2-$, $-CH_2OCH_2CHOHCH_2-$, $-CH_2(OCH_2CH_2)_y-$ or carbonyl where y is 1 to 10;

Q is a direct bond, $-CONH-R-NHCO-$ or $-ACONH-R-NHCO-$ where A is oxo or imino and R is a divalent aliphatic group having from 2 to 14 carbon atoms, a divalent 5- or 6-membered cycloaliphatic group having 5 to 14 carbon atoms or an arylene group having 6 to 14 carbon atoms, and wherein the A of Q is attached to X;

L is $-A(C_mH_{2m}O)_nC_mH_{2m}AY$ or La, where Y is a direct bond when L is divalent or hydrogen when L is monovalent, and m is 2 to 4 or a mixture thereof and n is 5 to 100; wherein A is as hereinbefore defined;

T is $-CONH-R_5A-$ or $-CONH-R-NHCOOR_5A-$ or $-CONH-R-NHCO-A-$ or $-R_5A-$ or a direct bond where A thereof is attached to E, where R₅ is alkylene or hydroxy-substituted alkylene of 2 to 15 carbon atoms and A and R are as hereinbefore defined;

E is $-CO-C(R_1)=CHR_2$ or $-CONH-phenyl-C(R_1)=CHR_2$ or $-CONH-C(R_4)_2-phenyl-C(R_1)=CHR_2$

where R₁ is hydrogen or methyl, and R₂ is hydrogen, methyl or $-COOR_3$,

where R₃ is hydrogen or alkyl of 1 to 4 carbon atoms with the proviso that, when R₁ is methyl, R₂ is hydrogen; and wherein R₄ is hydrogen or methyl;

G is $-(C_aF_{2a}O)_b-CF_2[CH_2-OCONH-R-NHCOOCH_2CF_2(OC_aF_{2a}O)_b]_x-$ or $-(C_aF_{2a}O)_b-CF_2[CH_2NHCONH-R-NHCONHCH_2CF_2(OC_aF_{2a}O)_b]_x-$ where x is 1 to 3; and a, b and R are as above; and

La is $-A(C_mH_{2m}O)_n[C_mH_{2m}ACONH-R-NHCOA(C_mH_{2m}O)_n]_zC_mH_{2m}AY$

where na is 5 to 100, z is 1 to 10 and Y is a direct bond when La is divalent or hydrogen when La is monovalent, and A, R, m and n are as hereinbefore defined.

2. A macromer according to claim 1, wherein X is $-CH_2-$ or $-CH_2(OCH_2CH_2)_y-$ where y is 1 or 2.

3. A macromer according to claim 1 wherein Q is $-ACONH-R-NHCO-$ where R is the radical derived from hexane-1,6-diisocyanate, trimethyl-hexane-1,6-diisocyanate, tetramethylene-diisocyanate, phenylene-1,4-diisocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, m- or p-tetramethylxylenediisocyanate,

isophorone diisocyanate or cyclohexane-1,4-diisocyanate.

4. A macromer according to claim 3 wherein R is the divalent radical derived from isophorone diisocyanate.

5. A macromer according to claim 1 where in Z, a is 1 or 2, and b is 3 to 50.

6. A macromer according to claim 1 where L is $-O(C_mH_{2m}O)_nC_mH_{2m}O-$ where m is 2 or a mixture of 2 and 3, and n is 10-50.

7. A macromer according to claim 1 where T is $-\text{CONH-R}_5\text{A}-$ and R_5 is ethylene and A is oxa.

8. A macromer according to claim 1 where T is $-\text{CONH-R-NHCOOR}_5\text{A}-$ and R_5 is ethylene and R is the radical derived from isophorone diisocyanate and A is oxa.

9. A macromer according to claim 1 where E is $-\text{CO-C(R}_1)=\text{CHR}_1$ where R_1 is methyl and R_2 is hydrogen.

10. A macromer according to claim 1 where E is $-\text{CONH-phenyl-C(R}_1)=\text{CHR}_2$ where R_1 and R_2 are both hydrogen.

11. A macromer according to claim 1 where in G, x is 1 and R is a radical derived from isophorone diisocyanate.

12. A macromer according to claim 1 where in La, A is oxa, R is a radical derived from isophorone diisocyanate, z is 1 to 5 and na is 5 to 100.

13. A macromer according to claim 1 having the formula (Ia)
E-T-L-Q-X-Z-X-Q-L-T-E.

14. A macromer according to claim 13 wherein

E is $-\text{CO-C(CH}_3)=\text{CH}_2$,

T is $-\text{CONH-CH}_2\text{CH}_2\text{-O-}$,

L is $-\text{O(C}_2\text{H}_4\text{O)}_n\text{C}_2\text{H}_4\text{O-}$ where n is 19-25,

Q is $-\text{OCONH-isophorone-NHCO-}$,

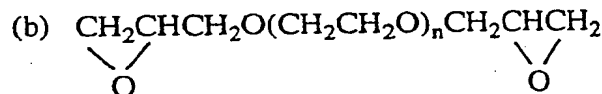
X is $-\text{CH}_2-$, and

Z is $-\text{CF}_2\text{O(C}_2\text{F}_4\text{O)}_r\text{-(CF}_2\text{O)}_s\text{-CF}_2-$ where

r:s is in the range of 1:10 to 5:1 and is preferably about 0.7.

15. A macromer according to claim 1 prepared by endcapping

(a) $\text{HOCH}_2(\text{C}_a\text{F}_{2a}\text{O})_b\text{-CF}_2\text{-CH}_2\text{OH}$ where a is 1 to 4 and b is 2 to 200 with



where n is 5 to 100 followed by reaction with

(c) 2-isocyanatoethyl methacrylate wherein the reactants a:b:c are in a 1:2:2 molar ratio.

16. A crosslinked homopolymerization product of a macromer

E-T-L-Q-X-Z-X-Q-L-T-E or

E-T-L-Q-X-G-X-Q-L-T-E

according to claim 1.

17. A crosslinked product according to claim 16 wherein the macromer is

E-T-L-Q-X-Z-X-Q-L-T-E where

E is $-\text{CO-C(CH}_3)=\text{CH}_2$,

T is $-\text{CONH-CH}_2\text{CH}_2\text{-O-}$,

L is $-\text{O(C}_2\text{H}_4\text{O)}_n\text{C}_2\text{H}_4\text{O-}$ where n is 19-25,

Q is $-\text{OCONH-isophorone-NHCO-}$,

X is $-\text{CH}_2-$, and

Z is $-\text{CF}_2\text{O(C}_2\text{F}_4\text{O)}_r\text{-(CF}_2\text{O)}_s\text{-CF}_2$ where

r:s is in the range of 1:10 to 5:1 and is preferably about 0.7.

18. A crosslinked copolymerization product of the macromer

E-T-L-Q-X-Z-X-Q-L-T-E or

E-T-L-Q-X-Z-X-Q-L

according to claim 1.

19. A product according to claim 18 where more than 1 % of the material, preferably more than 10 % of the material is derived from the macromer E-T-L-Q-X-Z-X-Q-L-T-E.

20. A product according to claim 18 where more than 20 % of the material, preferably more than 30% of the material is derived from the macromer E-T-L-Q-X-Z-X-Q-L-T-E.

21. A crosslinked homopolymerization product of the macromer of claim 15.
22. A method of preparing a hydrogel contact lens by crosslinking a macromer according to claim 1 in an inert solvent in a mold by free radical polymerization and equilibrating the resulting solvent swollen crosslinked contact lens in an aqueous medium.
- 5 23. A method according to claim 22 wherein the solvent is a lower alkanol, N,N-dimethylformamide, acetamide, acetonitrile, N,N-dimethylacetamide, dimethyl sulfoxide, acetone, tert-butyl acetate, isopropyl acetate or mixtures thereof.
24. A method according to claim 23 wherein the solvent is isopropyl acetate.
25. An ophthalmic device made according to claim 22.
- 10 26. An ophthalmic device prepared from the product of claim 16.
27. An ophthalmic device prepared from the product of claim 17.
28. An ophthalmic device prepared from the product of claim 18.
29. An ophthalmic device prepared from the product of claim 21.
30. A hydrogel contact lens made according to claim 22.
- 15 31. A hydrogel contact lens made according to claim 22 with greater than 20 % water content, preferably with greater than 30 % water content.
32. A hydrogel contact lens made according to claim 22 with greater than 40 % water content, preferably with greater than 50 % water content.
33. A hydrogel contact lens made according to claim 22 with between 25 and 55 % water content.
- 20 34. A contact lens according to claim 26.
35. A contact lens according to claim 27.
36. A contact lens according to claim 28.
37. A contact lens according to claim 29.
38. A crosslinked polymer which is the addition polymerization product of (a) a macromer containing
- 25 perfluoropolyalkylether and polyalkylether segments and ethylenically unsaturated moieties, having the formula I, more specifically as seen in formulas Ia to Id,
- E-T-L-Q-X-Z-X-Q-L-T-E, (Ia)
- E-T-L-Q-X-Z-X-Q-L, (Ib)
- E-T-L-Q-X-G-X-Q-L-T-E, (Ic)
- 30 E-T-L-Q-X-G-X-Q-L, (Id)
- wherein
- Z is $-(C_aF_{2a}O)_b-CF_2-$, where a is 1 to 4 or a mixture thereof and b is 2 to 200; X is a direct bond, $-CH_2-$, $-CH_2OCH_2CHOHCH_2-$, $-CH_2(OCH_2CH_2)_y-$ or carbonyl where y is 1 to 10;
- Q is a direct bond, $-CONH-R-NHCO-$ or $-ACONH-R-NHCO-$ where A is oxa or imino and R is a divalent
- 35 aliphatic group having from 2 to 14 carbon atoms, a divalent 5- or 6-membered cycloaliphatic group having 5 to 14 carbon atoms or an arylene group having 6 to 14 carbon atoms, and wherein the A of Q is attached to X;
- L is $-A(C_mH_{2m}O)_nC_mH_{2m}AY$ or La, where Y is a direct bond when L is divalent or hydrogen when L is monovalent, and m is 2 to 4 or a mixture thereof and n is 5 to 100;
- 40 wherein A is as hereinbefore defined;
- T is $-CONH-R_5A-$ or $-CONH-R-NHCOOR_5A-$ or $-CONH-R-NHCO-A-$ or $-R_5A-$ or a direct bond where A thereof is attached to E, where R_5 is alkylene or hydroxy-substituted alkylene of 2 to 15 carbon atoms and A and R are as hereinbefore defined;
- E is $-CO-C(R_1)=CHR_2$ or $-CONH-phenyl-C(R_1)=CR_2H$ or $-CONH-C(R_4)_2-phenyl-C(R_1)=CHR_2$
- 45 where R_1 is hydrogen or methyl, and R_2 is hydrogen, methyl or $-COOR_3$,
- where R_3 is hydrogen or alkyl of 1 to 4 carbon atoms with the proviso that, when R_1 is methyl, R_2 is hydrogen; and wherein R_4 is hydrogen or methyl;
- G is $-(C_aF_{2a}O)_b-CF_2[CH_2-OCONH-R-NHCOOCH_2CF_2(OC_aF_{2a})_b]_x-$ or $-(C_aF_{2a}O)_b-CF_2[CH_2-NHCONH-R-NHCONHCH_2CF_2(OC_aF_{2a})_b]_x-$ where x is 1 to 3; and a, b and R are as above; and
- 50 La is $-A(C_mH_{2m}O)_n[C_mH_{2m}ACONH-R-NHCOA(C_mH_{2m}O)_{na}]_zC_mH_{2m}AY$
- where na is 5 to 100, z is 1 to 10 and Y is a direct bond when La is divalent or hydrogen when La is monovalent, and A, R, m and n are as hereinbefore defined and
- b) a vinylic comonomer which is
- (i) a hydrophilic vinylic monomer,
- 55 (ii) a hydrophobic vinylic monomer,
- (iii) a polyreactive crosslinking agent,
- or (iv) a mixture of one or more (i), (ii) and (iii).
39. A polymer according to claim 38 wherein the hydrophilic vinylic monomer is selected from hydroxy-

substituted lower alkyl acrylates and methacrylates, acrylamide, methacrylamide, C₁-C₂ lower alkyl acrylamide and methacrylamide, ethoxylated acrylates and methacrylates, hydroxy substituted lower alkyl acrylamide and methacrylamide, hydroxy substituted lower alkyl vinyl ethers, sodium ethylene sulfonate, sodium styrenesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, N-vinylpyrrole, N-vinylsuccinimide, N-vinylpyrrolidone, 2- and 4-vinylpyridine, acrylic acid, methacrylic acid, amino (by amino including quaternary ammonium), -monoloweralkylamino- or diloweralkylamino- lower alkyl acrylates or methacrylates and allyl alcohol;

the hydrophobic vinylic monomer is selected from C₁ to C₁₈ alkyl acrylates and methacrylates, C₃ to C₁₈ alkyl acrylamides and methacrylamides, acrylonitrile, methacrylonitrile, vinyl C₁ to C₁₈ alkanates, C₂ to C₁₈ alkenes, C₂ to C₁₈ haloalkenes, styrene, C₁ to C₆ alkyl styrenes, vinyl alkyl ethers wherein the alkyl portion has 1 to 6 carbon atoms, C₃-C₁₂ perfluoroalkyl ethyl thiocarbonylaminoethyl acrylates and methacrylates, C₃-C₁₂ fluoroalkyl acrylates and methacrylates, acryloxy and methacryloxy-alkyl-siloxanes, N-vinylcarbazole, C₁-C₁₂ alkyl esters of maleic, fumaric, itaconic, and mesaconic acids; and the polyreactive crosslinking agent is selected from allyl methacrylate, diallyl itaconate, monoallyl itaconate, diallyl maleate, diallyl fumarate, diallyl succinate, diallyl phthalate, triallyl cyanurate, triallyl isocyanurate, diethylene glycol bis-allyl carbonate, triallyl phosphate, triallyl trimellitate, allyl ether, N,N-diallylmelamine; divinyl benzene, N,N'-methylene-bis-acrylamide, ethylene glycol dimethacrylate, neopentylglycol dimethacrylate, tetraethylene glycol dimethacrylate, hexamethylene-bis-maleimide, divinyl urea, bisphenol A bis methacrylate, divinyl adipate, glycerin trimethacrylate, trimethylolpropane triacrylate, trivinyl trimellitate, 1,5-pentadiene, 1,3-bis(4-methacryloxybutyl) tetramethyl disiloxane, divinyl ether, divinyl sulfone; and the dimethacrylate formed by reacting perfluoropolyalkylether dimethanol or poly(ethylene glycol) with two moles of isocyanatoethyl methacrylate.

40. A polymer according to claim 38 where in macromer (a), X is -CH₂- or -CH₂(OCH₂CH₂)_y- where y is 1 or 2.

41. A polymer according to claim 38 where in macromer (a), Q is -ACONH-R-NHCO- where R is the radical derived from hexane-1,6-diisocyanate, trimethyl-hexane-1,6-diisocyanate, tetramethylene-diisocyanate, phenylene-1,4-diisocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, m- or p-tetramethylxylenediisocyanate, isophorone diisocyanate or cyclohexane-1,4-diisocyanate.

42. A polymer according to claim 41 wherein R is the divalent radical derived from isophorone diisocyanate.

43. A polymer according to claim 38 where in macromer (a), a is 1 or 2, and b is 3 to 50.

44. A polymer according to claim 38 where in macromer (a), L is -O(C_mH_{2m}O)_nC_mH_{2m}O- where m is 2 or a mixture of 2 and 3, and n is 10-50.

45. A polymer according to claim 38 where in macromer (a), T is -CONH-R₅A- and R₅ is ethylene and A is oxa.

46. A polymer according to claim 38 where in macromer (a), T is -CONH-R-NHCOOR₅A- and R₅ is ethylene and R is the radical derived from isophorone diisocyanate and A is oxa.

47. A polymer according to claim 38 where in macromer (a), E is -CO-C(R₁)=CHR₂ where R₁ is methyl and R₂ is hydrogen.

48. A polymer according to claim 38 where in macromer (a), E is -CONH-phenyl-C(R₁)=CHR₂ where R₁ and R₂ are both hydrogen.

49. A polymer according to claim 38 where in macromer (a), x is 1 and R is a radical derived from isophorone diisocyanate.

50. A polymer according to claim 38 where in La of macromer (a), A is oxa, R is a radical derived from isophorone diisocyanate, z is 1 to 5 and na is 5 to 100.

51. A polymer according to claim 38 where the macromer (a) has the formula (Ia)

E-T-L-Q-X-Z-X-Q-L-T-E.

52. A polymer according to claim 51 where in the macromer (a),

E is -CO-C(CH₃)=CH₂,

53. T is -CONH-CH₂CH₂-O-

, L is O(C₂H₄O)_nC₂H₄O- where n is 19-25,

Q is -OCONH-isophorone-NHCO-,

X is -CH₂-, and

Z is -CF₂O(C₂F₄O)_r-(CF₂O)₅-CF₂- where

54. r:s is in the range of 1:10 to 5:1 and is preferably about 0.7.

55. A crosslinked polymer according to claim 38 wherein (b) is up to 10 % by weight.

56. A crosslinked polymer according to claim 53 wherein (b) is 2-hydroxyethyl methacrylate, N-vinylpyrrolidone, N,N-dimethylacrylamide, ethylene glycol dimethacrylate, the reaction product of poly-

(ethylene glycol) with two moles of 2-isocyanatoethyl methacrylate or the reaction product of perfluoropolyalkylether dimethanol with two moles of 2-isocyanatoethyl methacrylate.

55. A method of preparing a hydrogel contact lens by crosslinking a macromer (a) with a vinylic comonomer (b) according to claim 38 in an inert solvent in a mold by free radical polymerization and
5 equilibrating the resulting solvent swollen crosslinked contact lens in an aqueous medium.

56. A method according to claim 55 wherein the solvent is a lower alkanol, N,N-dimethylformamide, acetamide, acetonitrile, N,N-dimethylacetamide, dimethyl sulfoxide, acetone, tert-butyl acetate, isopropyl acetate or mixtures thereof.

57. A method according to claim 56 wherein the solvent is isopropyl acetate.

10 58. An ophthalmic device made according to claim 55.

59. An ophthalmic device prepared from the product of claim 38.

60. An ophthalmic device prepared from the product of claim 51.

61. An ophthalmic device prepared from the product of claim 52.

62. An ophthalmic device prepared from the product of claim 53.

15 63. An ophthalmic device prepared from the product of claim 54.

64. A contact lens according to claim 59.

65. A contact lens according to claim 60.

66. A contact lens according to claim 61.

67. A contact lens according to claim 62.

20 68. A contact lens according to claim 63.

69. A hydrogel contact lens made according to claim 55.

70. A hydrogel contact lens made according to claim 55 with greater than 20 % water content, preferably with greater than 30 % water content.

71. A hydrogel contact lens made according to claim 55 with greater than 40 % water content,
25 preferably with greater than 50 % water content.

72. A hydrogel contact lens made according to claim 55 with between 25 and 55 % water content.

73. The use of a macromer according to claim 1 for making a contact lens.

74. The use of a polymer according to claim 38 for making a contact lens.

30

35

40

45

50

55



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 379 462 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90810002.7

(22) Date of filing: 04.01.90

(51) Int. Cl.⁵: **C08G 18/81**, C08G 18/50,
C08G 18/38, C08G 18/10,
C08G 18/48, C08F 299/06,
G02B 1/04, C08G 65/32

(30) Priority: 11.01.89 US 296169
11.01.89 US 296170

(43) Date of publication of application:
25.07.90 Bulletin 90/30

(64) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(88) Date of deferred publication of the search report:
23.10.91 Bulletin 91/43

(71) Applicant: **CIBA-GEIGY AG**
Klybeckstrasse 141
CH-4002 Basel(CH)

(72) Inventor: **Goldenberg, Merrill**
626 Kent Avenue
Teaneck, N.J. 07666(US)

(54) **Vinylic macromers containing perfluoropolyalkylether and polyalkylether segments, polymers, copolymers and ophthalmic devices made therefrom.**

(57) The instant invention relates to vinylic macromers containing perfluoropolyalkylether and polyalkylether segments, polymers and ophthalmic devices such as intraocular implants and contact lenses and particularly soft hydrogel contact lenses made therefrom, and to crosslinked copolymers of (a) said vinylic macromers containing perfluoropolyalkylether and polyalkylether segments with (b) minor amounts of vinylic comonomers and ophthalmic devices such as intraocular implants and contact lenses and particularly soft hydrogel contact lenses made therefrom.

EP 0 379 462 A3



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 81 0002

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 273 449 (AUSIMONT) * Claims 1,5,7; page 4, line 16 - page 5, line 45 *	1	C 08 G 18/81 C 08 G 18/50 C 08 G 18/38
A	EP-A-0 322 624 (SIEMENS) * Claims 1-5 *	1	C 08 G 18/10 C 08 G 18/48 C 08 F 299/06 G 02 B 1/04 C 08 G 65/32
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 G C 08 F G 02 B
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 08 August 91	Examiner VAN PUymbroeck M.A.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div> <div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</div>			

BEST AVAILABLE COPY